





### DOE/NETL's Carbon Capture R&D Program for Existing Coal-Fired Power Plants

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#### **Abstract**

Coal-fired power plants have continued to make significant progress in reducing emissions of sulfur and nitrogen oxides (SOx and NOx), particulate matter, and mercury since passage of the 1970 Clean Air Act. However, there is a possibility that carbon dioxide (CO<sub>2</sub>) emissions could also be regulated in the near future to address climate change. Recognizing that current CO<sub>2</sub> capture technology is not cost-effective and has not been demonstrated at scale, the U.S Department of Energy's National Energy Technology Laboratory (DOE/NETL) has initiated a research and development (R&D) program directed specifically at post- and oxy-combustion CO<sub>2</sub> capture technologies that can be retrofit to existing coal-fired power plants, as well designed into new plants. The goal of the DOE/NETL effort, which is being carried out as part of the Existing Plants, Emissions and Capture (EPEC) Program, is to develop advanced CO<sub>2</sub> capture and compression technologies for both existing and new coal-fired power plants that when combined can achieve 90 percent CO<sub>2</sub> capture at less than a 35 percent increase in cost of electricity (COE). An aggressive R&D plan has been established in order to develop multiple CO<sub>2</sub> capture technology options, capable of meeting the cost and performance target, at a commercial scale by 2020.

#### Introduction

Coal-fired power plants generate more than 50 percent of the electricity in the United States. DOE's Energy Information Administration projects that the more than 300 gigawatts (GW) of coal-fired electricity generating capacity currently in operation will increase to over 400 GW by 2030 (1). However, electricity production from fossil fuel-based power plants will be challenged by growing concerns that anthropogenic emission of greenhouse gases (GHG), such as CO<sub>2</sub>, are contributing to global climate change. The existing fleet of coal-fired power plants emits about two billion tons of CO<sub>2</sub> annually, accounting for roughly two-thirds of the total CO<sub>2</sub> emissions in the U.S. power sector. Moreover, as shown in Figure 1, more than 90 percent of the coal-fired CO<sub>2</sub> emissions projected to be released from 2007 through 2030 will originate from today's existing coal-fired power plants as less than 4 GW of capacity is projected to retire during that period (1).

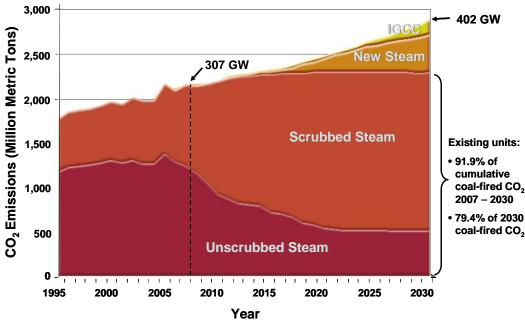


Figure 1: U.S. Coal-Fired Electric Power Generation Carbon Dioxide Emission Projections

While a technological portfolio will be necessary to stabilize global GHG emissions (2),<sup>2</sup> carbon capture and storage (CCS) represents a promising option for directly reducing CO<sub>2</sub> emissions from coal-fired power plants. Under an integrated CCS concept, CO<sub>2</sub> would be captured, compressed, transported via pipeline, and permanently stored and monitored in geologic formations, such as depleted oil and gas fields, saline formations, and unmineable coal seams (3).<sup>3</sup> DOE/NETL has been dedicated to advancing all aspects of CCS systems for over a decade (4),<sup>4</sup> but this paper will focus primarily on the CO<sub>2</sub> capture R&D tailored for the existing fleet. The two general approaches for capture at existing plants are post- and oxy-combustion.

#### **Background**

Post-combustion CO<sub>2</sub> capture, or separation of CO<sub>2</sub> produced by conventional coal combustion in air, presents technical challenges since the flue gas is at atmospheric pressure and the CO<sub>2</sub> concentration is 10 to 15 volume percent, resulting in a low CO<sub>2</sub> partial pressure and a large volume of gas to be treated. In spite of this difficulty, post-combustion CO<sub>2</sub> capture offers the greatest near-term potential for reducing GHG emissions because it can be retrofitted to existing units and can also be tuned for various levels of CO<sub>2</sub> capture, which may accelerate market acceptance.

The limited chemical potential for separating CO<sub>2</sub> from existing power plant flue gas streams supports the use of chemical processes, such as amine-based scrubbing with an aqueous monoethanolamine (MEA) solution (Figure 2), which are capable of achieving high levels of CO<sub>2</sub> capture (90% or more) from flue gas due to fast kinetics and strong chemical reactions. However, off-the-shelf amine solvents are corrosive, susceptible to degradation by trace flue gas constituents (particularly SOx), and necessitate significant amounts of energy, in the form of low-pressure steam, for sensible heating, heat of reaction, and stripping for CO<sub>2</sub> regeneration. In fact, DOE/NETL has estimated that MEA-based CCS will increase the COE for a new

pulverized coal (PC) plant by about 80 to 85 percent, and even more for retrofits, while reducing the power plant net efficiency by about 30 percent (5,6). Further, although MEA-based scrubbing has been utilized for over 60 years for natural gas purification and food-grade CO<sub>2</sub> production, it has not been demonstrated at the larger-scale necessary for 90 percent CO<sub>2</sub> capture at a 500-MW coal-fired power plant where 10,000 to 15,000 tons of CO<sub>2</sub> would be removed per day.

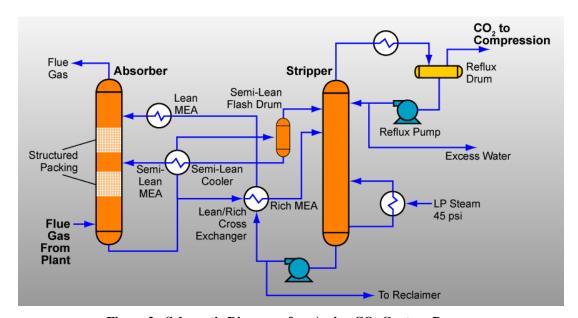


Figure 2: Schematic Diagram of an Amine CO<sub>2</sub> Capture Process

With the potential of large-scale power plant CO<sub>2</sub> mitigation on the horizon, technology developers, such as Fluor Corporation (Econamine FG Plus<sup>SM</sup>) and Mitsubishi Heavy Industries (KM-CDR Process), have begun to optimize chemical scrubbing technology (7,8).<sup>7,8</sup> The modifications are focused primarily on extensive thermal integration of the CO<sub>2</sub> capture system with the power plant and the development of improved solvent formulations with lower stripping steam requirements and lower solvent circulation rates than MEA (9).<sup>9</sup> These process improvements have potential to decrease the cost and energy-intensity of post-combustion CO<sub>2</sub> capture, which is estimated to account for about three-fourths of the total cost of an integrated CCS system.

PC oxy-combustion power plants are designed to utilize high-purity oxygen  $(O_2)$  mixed with recycled flue gas (primarily  $CO_2$ ) to combust coal and produce a highly concentrated  $CO_2$  stream (greater than 60 percent by volume). The  $CO_2$  is further purified by condensing the water  $(H_2O)$  vapor through the use of cooling, desiccant systems, and compression to a dew point of  $-40^{\circ}F$ . Depending on the end-use and pipeline specification, additional treatment may be necessary to reduce other gas constituents  $(O_2$ , SOx and NOx). Although PC oxy-combustion is a relatively new concept and experience with integrated systems is limited, most key process components, including the cryogenic air separation unit (ASU) for  $O_2$  production are proven and commercially-available. PC oxy-combustion is currently being evaluated at the 30 megawatt thermal  $(MW_{th})$  scale by Babcock & Wilcox Company (B&W) and Vattenfall (10,11).

However, the appeal of oxy-combustion is tempered by a few key challenges, namely the capital cost and energy consumption for cryogenic ASU operation, boiler air infiltration that dilutes the flue gas with nitrogen ( $N_2$ ), and excess  $O_2$  contained in the concentrated  $CO_2$  stream. Flue gas recycle (approximately 70 to 80 percent) is also necessary to approximate the combustion characteristics of air since currently-available boiler materials cannot withstand the high temperatures resulting from coal combustion in pure  $O_2$  (I2). Consequently, the economic benefit of oxy-combustion compared to amine-based scrubbing systems is limited. In comparison to a supercritical PC plant without CCS, DOE/NETL estimates that a new oxy-fired supercritical PC plant would incur a COE increase of about 60 percent (6).

Given the significant economic penalties associated with current CO<sub>2</sub> capture technologies, stepchange improvements in both cost and energy efficiency will be required to ensure that CCS for existing plants can be done at costs and impacts that are economically-acceptable.

#### DOE/NETL's Carbon Capture for Existing Plants R&D Program

The EPEC Program is conducting R&D on advanced post- and oxy-combustion CO<sub>2</sub> capture technologies, and novel CO<sub>2</sub> compression techniques for existing coal-fired power plants. In addition to funding external R&D projects, DOE/NETL also conducts in-house research through the Office of Research and Development (ORD) to develop new breakthrough concepts for CO<sub>2</sub> capture that could lead to dramatic improvements in cost and performance relative to today's technologies. The EPEC CO<sub>2</sub> emissions control R&D activity also sponsors systems analysis studies of the cost and performance of CO<sub>2</sub> capture technologies (5,6). The EPEC Program goal is to develop post- and oxy-combustion capture technologies for new and existing coal-fired power plants that achieve 90 percent CO<sub>2</sub> capture at less than a 35 percent increase in COE and are available for commercial deployment by 2020.

In support of this goal, DOE/NETL on July 31, 2008 announced that it will provide \$36 million for 15 new laboratory- through pilot-scale post- and oxy-combustion CO<sub>2</sub> capture R&D projects. These projects (denoted by an asterisk in Table 1) will build upon the current portfolio of CO<sub>2</sub> capture research that was initiated in 2006 under DOE/NETL's Carbon Sequestration Program and focus on five technology pathways: solvents, sorbents, and membranes for post-combustion CO<sub>2</sub> capture, oxy-combustion (flue gas purification and boiler development), and chemical looping combustion (CLC). DOE/NETL is developing a broad portfolio of CO<sub>2</sub> capture technologies for the existing fleet to accommodate differences in plant age, size, configuration, and other site-specific factors like available space and ductwork design.

Table 1: DOE/NETL Current CO<sub>2</sub> Capture Technology R&D Projects

	<b>Project Focus</b>	Participant	Project Focus	Participant	
Post-Combustion Solvents	High-Capacity Oligomers*	GE Global Research	PC Oxy-Combustion Pilot Testing	Babcock & Wilcox	Oxy-Combustion
	Integrated Vacuum Carbonate Absorption Process*	Illinois State Geological Survey	Oxy-Combustion Impacts in Existing Coal-Fired Boilers*	Reaction Engineering International	
	Phase Transitional Absorption	Hampton University	Oxy-Combustion Boiler Development for Tangential Firing*	Alstom Power	
	Ionic Liquids	University of Notre Dame	Oxy-Combustion Boiler Material Development*	Foster Wheeler NA, Corp.	
	Reversible Ionic Liquids*	Georgia Tech Research Corp.	Oxy-Combustion CO <sub>2</sub> Recycle Retrofit	Southern Research Institute	
Post-Combustion Sorbents	Amine-Grafted Zeolites	University of Akron	Pilot-Scale Oxy-Fuel Research	CANMET	
	Dry Carbonate Process	Research Triangle Institute (RTI)	PC Oxy-Combustion with Integrated Pollutant Removal	Jupiter Oxygen Corporation	
	Low-Cost CO <sub>2</sub> Sorbent*	TDA Research	Evaluation of CO <sub>2</sub> Capture/Utilization/Disposal Options	Argonne National Laboratory	
	Metal Organic Frameworks	UOP LLC	Flue Gas Purification using SOx/NOx Reactions during CO <sub>2</sub> Compression*	Air Products and Chemicals, Inc.	
	Carbon Sorbents*	SRI International	Near-Zero Emissions Oxy- Combustion Flue Gas Purification*	Praxair, Inc.	
	Solid Sorbents*	ADA-ES, Inc.	Oxy-Combustion with CO <sub>2</sub> Capture	DOE/NETL's ORD	
	Reactor Design Studies	DOE/NETL's ORD	Oxy-Fired Combustion Simulation	DOE/NETL's ORD	
	Carbon-Supported Amine Sorbents	DOE/NETL's ORD	Materials Performance in Oxy- Combustion Environments	DOE/NETL's ORD	
	Supported Amine Sorbent Modeling	DOE/NETL's ORD	Oxy-Fuel Flame Property Measurement	DOE/NETL's ORD	
	CO <sub>2</sub> Capture Sorbent-Based Device Simulation	DOE/NETL's ORD	Wireless Sensing in Oxy-Fuel Environments	DOE/NETL's ORD	
	Surface Immobilization Nanotechnology for Sorbents	DOE/NETL's ORD	Oxygen Transport Membrane-Based Oxy-Combustion	Praxair, Inc.	O <sub>2</sub> Supply
	CO <sub>2</sub> Sorbent Development	DOE/NETL's ORD	CLC Prototype*	Alstom Power, Inc.	)
Post-Combustion Membranes	Biomimetic Membrane	Carbozyme, Inc.	Coal Direct Chemical Looping*	Ohio State University	Chemical Looping Combustion
	CO <sub>2</sub> Membrane Process*	RTI	CLC Oxygen Carrier Studies	DOE/NETL's ORD	
	Membrane Process for CO <sub>2</sub> Capture*	Membrane Technology & Research (MTR)	CLC Model Development	DOE/NETL's ORD	
	Novel Dual-Functional Membrane	University of New Mexico	Laboratory-Scale CLC Combustor	DOE/NETL's ORD	
	Novel Polymer Membranes	MTR	Design and Control of CLC Systems	DOE/NETL's ORD	'n
	Electrochemical Membranes	DOE/NETL's ORD	Novel Concepts for CO <sub>2</sub> Compression	Southwest Research Institute	Com
All	Power Systems Development Facility – Carbon Research Center	Southern Company	Supersonic Shock Wave Compression Technology	Ramgen Power Systems	Compression

#### **Solvents**

Solvent-based CO<sub>2</sub> capture involves chemical or physical sorption of CO<sub>2</sub> from flue gas into a liquid carrier. As discussed previously, solvent-based systems are in commercial use today scrubbing CO<sub>2</sub> from industrial flue gases and process gases; however, they have not been applied to removing large volumes of CO<sub>2</sub>, as would be encountered in the flue gas from existing coal-fired power plants. Research projects in this pathway address technical challenges to solvent-based CO<sub>2</sub> capture, such as large flue gas volume, relatively low CO<sub>2</sub> concentration, flue gas contaminants, and high parasitic power demand for solvent recovery.

#### **Chemical Solvents**

Chemical absorption involves one or more reversible chemical reactions between CO<sub>2</sub> and an aqueous solution of an absorbent, such as an alkanolamine (e.g., MEA), hindered amine, aqueous ammonia, or a carbonate, to form water-soluble compounds. Chemical solvents are able to capture high levels of CO<sub>2</sub> from flue gas streams with a low CO<sub>2</sub> partial pressure due to chemical reactivity, but capacity is equilibrium-limited. Thus, chemical solvent-based systems incur a significant cost and efficiency penalty during the regeneration step, which involves a temperature swing to break the absorbent-CO<sub>2</sub> chemical bond. DOE/NETL is investigating advanced solvents that have lower regeneration heat duties than MEA, and that are also resistant to flue gas impurities. Previous research focused on potassium carbonate promoted with piperazine (*13*), while future work will evaluate an integrated vacuum carbonate absorption process (*14*)<sup>14</sup> and novel oligomeric solvents.

#### **Taking the Next Step**

DOE/NETL ORD researchers developed and patented a novel ammonia solvent-based  $CO_2$  capture technology that relies upon a temperature swing to cycle between ammonium carbonate and ammonium bicarbonate. This reaction has a significantly lower heat of reaction than amine-based systems, resulting in energy savings, provided the absorption/desorption cycle can be limited to this mechanism. Ammonia-based absorption has a number of other advantages over amine-based systems, such as the potential for high  $CO_2$  capacity, lack of degradation during absorption/regeneration, tolerance to  $O_2$  in the flue gas, low cost, and potential for regeneration at high pressure.

Powerspan Corporation subsequently licensed the aqueous ammonia process in 2007 and rebranded it  $ECO_2^{\circledast}$ . Through integration with the  $ECO^{\circledast}$  multi-pollutant control system, Powerspan is currently conducting a 1-MW pilot test at FirstEnergy's R.E. Burger Power Station in Ohio. Powerspan has also announced plans to conduct full-scale demonstrations (120-MW) of the  $ECO_2^{TM}$  process at NRG Energy's W.A. Parish Power Plant in Texas and Basin Electric's Antelope Valley Station in North Dakota beginning in 2012 (15).

#### **Physical Solvents**

Another CO<sub>2</sub> capture process currently being used in smaller-scale industrial applications, physical absorption, is a bulk phenomenon where inorganic or organic liquids preferentially absorb a gaseous species from the gas mixture. Although physical solvent regeneration is less energy-intensive than chemical systems, this technology is considered more practical for

processing the high-pressure fuel gas generated at coal gasification plants since CO<sub>2</sub> solubility in physical solvents increases with partial pressure (16). 16

The University of Notre Dame and Georgia Tech, however, are investigating a new class of physical solvents that are designed to capture CO<sub>2</sub> from low-pressure flue gas streams. Ionic liquids (ILs) include a broad category of salts, typically containing an organic cation and either an inorganic or organic anion. ILs have essentially no vapor pressure and are thermally stable at temperatures up to several hundred degrees Centigrade, which minimizes solvent loss during CO<sub>2</sub> separation. Task-specific ILs containing amine functionality have been developed with CO<sub>2</sub> solubility 40 times greater than exhibited prior to the start of the DOE/NETL-funded R&D project. One possible drawback is that the high viscosity of many ILs could adversely affect the ability to pump ILs in a power plant application (17).<sup>17</sup>

#### **Sorbents**

Solid sorbents, including sodium and potassium oxides, zeolites, carbonates, amine-enriched sorbents, and metal organic frameworks (MOFs), are also being explored for CO<sub>2</sub> capture at existing plants. A temperature swing facilitates sorbent regeneration following chemical and/or physical adsorption, but a key attribute of CO<sub>2</sub> sorbents is that less H<sub>2</sub>O is present, compared to solvent-based systems, thereby reducing the sensible heating and stripping energy requirements. Possible configurations for contacting the flue gas with the sorbents include fixed, moving, and fluidized beds. Research projects in this pathway address key technical challenges to sorbent-based systems, such as solids circulation, sorbent attrition, low chemical potential, heat transfer, reactive flue gas contaminants, and the parasitic power and potential sweep gas demand for sorbent regeneration.

DOE/NETL ORD scientists have developed amine-enriched sorbents that are prepared by treating high surface area substrates with various amine compounds. The implanting of the amine on a solid substrate increases the surface contact area of the amine for CO<sub>2</sub> capture, thus requiring less sorbent/amine. This advantage, combined with the elimination of a H<sub>2</sub>O carrier, has the potential to improve the energy efficiency of the process compared to MEA scrubbing. Concurrently, DOE/NETL's ORD is evaluating novel reactor designs for large-scale, sorbent-based CO<sub>2</sub> capture systems applicable to new and existing PC power plants (18). <sup>18</sup>

Research Triangle Institute (RTI) International is investigating the use of supported-sodium carbonate (Na<sub>2</sub>CO<sub>3</sub> or soda ash) as an inexpensive and efficient CO<sub>2</sub> sorbent. The Na<sub>2</sub>CO<sub>3</sub> reacts with CO<sub>2</sub> and H<sub>2</sub>O to form sodium bicarbonate via a reversible reaction that requires a temperature swing from about 60°C to 120°C for sorbent regeneration. RTI's Dry Carbonate Process was successfully integrated into the U.S. Environmental Protection Agency's Multi-Pollutant Control Research Facility – a 4 MMBTU/hr bench-scale furnace. During a total of 105 hours of testing with coal-derived flue gas, the Dry Carbonate Process achieved 90 percent CO<sub>2</sub> capture. In comparison to MEA scrubbing, the Dry Carbonate Process offers four distinct economic advantages: (1) reduced capital costs; (2) lower auxiliary power load; (3) reduced steam turbine power de-rating; and (4) and lower reactive material costs (19).

UOP LLC is leading the DOE/NETL effort to develop MOFs - a class of materials that are thermally-stable, have adjustable chemical functionality that can be tailored for high  $CO_2$  adsorption capacity, and possess very high porosity. UOP has developed a Virtual High Throughput Screening model to reduce the number of MOF synthesis experiments to only those that have the highest probability of success. A wide variety of MOFs have been successfully synthesized (Figure 3) and preliminary results indicate that MOFs are hydrothermally-stable and capable of separating  $CO_2$  from simulated flue gas streams (20).

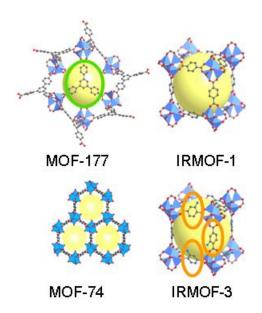


Figure 3: Illustration of MOFs Developed by the University of Notre Dame

#### **Membranes**

Membrane-based  $CO_2$  capture uses permeable or semi-permeable materials that allow for the selective transport and separation of  $CO_2$  from flue gas. Gas separation is accomplished by some physical or chemical interaction between the membrane and the gas being separated, causing one component in the gas to permeate through the membrane faster than another. In general, membrane processes offer the following advantages: (1) passive operation with no moving parts; (2) tolerant of chemical contaminants (SOx, NOx); (3) energy-efficient with low operating costs; and (4) small, modular footprint.

While membranes are more advantageous for separating  $CO_2$  in high-pressure applications, such as coal gasification, the EPEC Program is focused on developing highly-selective and permeable membrane systems designed specifically for  $CO_2$  separation from low partial pressure flue gas streams. For instance, gas absorption membranes, where separation is promoted by a hybrid membrane/absorption liquid (e.g., amine solvent or enzymes) combination that selectively removes  $CO_2$  from the flue gas stream (Figure 4), are a promising retrofit technology.

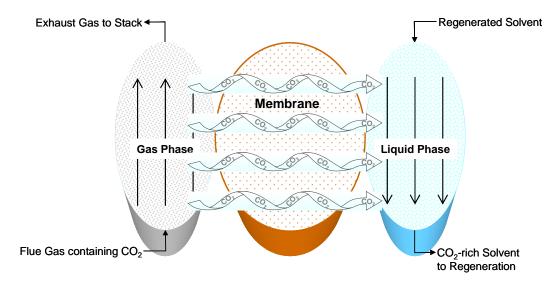


Figure 4: Schematic of a Gas Absorption Membrane

Membrane Technology and Research (MTR) for example, is investigating novel thin-film, composite polymer membranes and associated process configurations to increase the flux of CO<sub>2</sub> across the membrane, thereby reducing membrane area. A novel countercurrent design that utilizes a portion of the incoming combustion air as a sweep gas is being pursued to maximize the driving force for membrane permeation. Preliminary results indicate that 90 percent CO<sub>2</sub> capture at a 600-MW coal-fired power plant will require about 700,000 cubic meters of membrane, or 135 of MTR's nested module skids with a total footprint of about 0.5 acres (21). <sup>21</sup>

Another membrane process, under development by Carbozyme, leverages the carbonic anhydrase (CA) enzyme to catalyze the conversion of CO<sub>2</sub> to bicarbonate at the flue gas interface and reverses the process via a pressure swing at the CO<sub>2</sub> product interface. The Carbozyme permeator consists of two hollow-fiber, microporous membranes separated by a thin liquid membrane. CA is attached to the hollow-fiber wall to ensure that the incoming CO<sub>2</sub> contacts the CA at the gas-liquid interface to maximize conversion efficiency. While the CA process has been shown to have a low heat of absorption that reduces the energy penalty typically associated with absorption processes, potential technical limitations include membrane boundary layers, pore wetting, surface fouling, loss of enzyme activity, long-term operation, and scale-up, which are currently being addressed. The Carbozyme permeator system was validated recently during laboratory-scale testing on a 0.5 cubic meter permeator, in which, 85 percent removal of CO<sub>2</sub> from a 15.4 percent CO<sub>2</sub> feed stream was achieved. Upon fabrication, the next-scale permeator will be shipped to the Energy and Environmental Research Center for testing on coal combustion flue gas (22).<sup>22</sup>

#### **Oxy-combustion**

PC oxy-combustion involves the use of relatively pure  $O_2$  mixed with recycled flue gas (primarily  $CO_2$ ) for coal combustion to produce a concentrated  $CO_2$  stream. Experience with coal oxy-combustion is limited and therefore, continued R&D on oxy-combustion flame characteristics, burner and coal-feed design, and analyses of the interaction of oxy-combustion

products with boiler materials are necessary to ensure the development of low-cost and efficient oxy-combustion power plant systems. As a result, DOE/NETL is conducting laboratory- through pilot-scale R&D of the following oxy-combustion supporting processes:

- Advanced oxy-combustion boilers designed with new materials of construction to handle higher combustion flame temperatures and potentially higher sulfur concentrations for co-sequestration applications;
- Advanced oxy-burner designs to maintain a stable combustion flame;
- Novel O<sub>2</sub> separation/boiler integrated designs to reduce the cost of O<sub>2</sub> production; and
- Advanced flue gas purification and compression technologies.

B&W completed successful oxy-combustion testing at the 1.5-MW<sub>th</sub> scale and is currently operating a 30-MW<sub>th</sub> oxy-combustion pilot unit at B&W's Clean Environment Development Facility in Alliance, OH. Preliminary results indicate that flue gas volume is reduced by about 80 percent with  $CO_2$  concentrations greater than 80 percent achieved. Pilot-scale testing has also demonstrated a smooth transition between air- and oxy-firing modes, and led to the development of two near full-scale oxy-burners - B&W DRB-XCL® for eastern bituminous coal, and DRB-PAX<sup>TM</sup> for low-rank coals (*10*).

In 2004, Alstom Power conducted pilot-scale (3-MW<sub>th</sub>) testing of an oxygen-fired circulating fluidized bed (CFB) combustor with both bituminous coal and petroleum coke in  $O_2/CO_2$  mixtures containing up to 50 percent  $O_2$  by volume. The testing successfully addressed several technical issues, such as furnace operability, temperature control, heat transfer, recarbonation, criteria and trace gaseous emissions, and unburned carbon. The pilot-scale tests confirmed the operability and technical feasibility of an oxygen-fired CFB system. Alstom completed a conceptual design and economic analysis for the conversion of an existing 90-MW CFB unit to oxy-firing that indicated a cost of \$37 per ton of  $CO_2$  avoided (23).

#### **Oxygen Supply**

For oxy-combustion to be a cost-effective power generation option, a low-cost supply of pure  $O_2$  is required. Although a cryogenic ASU can be used to supply high-purity  $O_2$  to the boiler, this commercially-available technology is both capital- and energy-intensive (6). Novel  $O_2$  production technologies currently under development, such as ion transport membranes, have the potential to reduce the cost of  $O_2$  production.

Praxair, Inc. is investigating the design and operation of oxygen transport membranes (OTMs), which utilize chemical potential for the O<sub>2</sub> separation driving force instead of pressure. The OTMs are designed to integrate directly with the boiler such that the combustion reaction occurs on the fuel side of the membrane thus creating a low O<sub>2</sub> partial pressure driving force. This chemical potential gradient drives O<sub>2</sub> through the membrane without the need for additional air compression. In preparation for pilot-scale testing, a ceramic membrane and seal assembly has been developed for thermal integration between the high-temperature membrane and the combustion process. Prototype single- and multi-tube reactors have been built to demonstrate membrane performance and durability. Praxair estimates that OTMs can deliver O<sub>2</sub> for oxycombustion using only 20 to 30 percent of the energy required for a cryogenic ASU (24).

#### **Chemical Looping Combustion**

Another advanced coal oxy-combustion technology, known as chemical looping combustion (CLC), involves the use of a metal oxide or other compound as an  $O_2$  carrier to transfer  $O_2$  from the combustion air to the fuel. Since direct contact between fuel and combustion air is avoided (Figure 5), the products from combustion ( $CO_2$  and  $H_2O$ ) will be kept separate from the rest of the flue gases (primarily  $N_2$ ). CLC splits combustion into separate oxidation and reduction reactions. The metal oxide (e.g., iron, nickel, copper, or manganese) releases the  $O_2$  in a reducing atmosphere and the  $O_2$  reacts with the fuel. The metal is then recycled back to the oxidation chamber where the metal oxide is regenerated by contact with air. The primary advantage of the CLC process is that no separate ASU is required and  $CO_2$  separation takes place during combustion. Supporting R&D projects will advance the development of CLC systems by addressing key issues, such as solids handling and  $O_2$  carrier capacity, reactivity, and attrition (25,26).

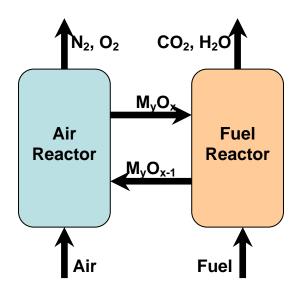


Figure 5: CLC Process Schematic

Under DOE/NETL support, Alstom Power is planning on installing and operating a 3-MW<sub>th</sub> CLC prototype at their existing Power Plant Laboratory in Windsor, CT. The prototype will utilize limestone as the O<sub>2</sub> carrier and include process loops to transfer solids and O<sub>2</sub> between the reducing and oxidation reactors. Information obtained from operation will be used to develop a technical plan and cost estimate for a subsequent commercial demonstration project at a full-scale power plant (27).<sup>27</sup>

#### CO<sub>2</sub> Compression

In preparation for pipeline transport and permanent storage (enhanced oil recovery, deep geologic formations), the concentrated CO<sub>2</sub> stream must be further dehydrated and compressed to a supercritical liquid (1,070 psi, 74 bar). DOE/NETL estimates that for a new 667-MW

supercritical PC power plant, multi-stage, centrifugal  $CO_2$  compression from the stripper regeneration column (20 to 25 psi) to 2,200 psi (pipeline pressure set by the NETL Systems Analysis Guidelines) would consume nearly 50 MW of auxiliary power, or about 0.1 MW per ton of  $CO_2$  (6).

Liquefaction of CO<sub>2</sub> to supercritical conditions can take place via two thermodynamic routes multi-stage compression with interstage cooling, or a combination of compression, cooling, and pumping to supercritical pressures. In pursuit of the latter approach, Southwest Research Institute is investigating the use of refrigeration to liquefy the CO<sub>2</sub> so that its pressure can be increased using a pump, rather than a compressor. The primary power requirements for the hybrid refrigeration approach are the initial compression to boost the CO<sub>2</sub> to approximately 250 psi and further refrigeration required to liquefy the gaseous CO<sub>2</sub>. Once the CO<sub>2</sub> is liquefied, the pumping power to boost the pressure to pipeline supply pressure is minimal.

Ramgen Power Systems is developing a supersonic shock wave compression technology that features a rotating disk operating at high peripheral speeds to generate shock waves that compress the CO<sub>2</sub>. There are several proposed advantages of the Rampressor compared to the conventional multi-stage or hybrid refrigeration approaches. First, shock compression employs only 2 stages of compression (versus 6 to 10 stages with a multi-stage approach) and therefore, offers potential capital cost savings up to 50 percent. In addition, the compressed CO<sub>2</sub> is recovered at higher temperatures (400°F to 600°F, depending on the efficiency) due to fewer stages (higher compression ratio), providing an opportunity for heat recovery through integration into either the power plant steam cycle or CO<sub>2</sub> capture process. Recent prototype testing has achieved a 7.8:1 compression ratio (28).<sup>28</sup>

#### **Summary**

DOE/NETL's EPEC Program is carrying out a comprehensive R&D effort directed at advancing the technical performance and cost-effectiveness of CO<sub>2</sub> capture technologies for new and existing coal-fired power plants. The program is focused on advanced post- and oxy-combustion capture technologies that can achieve 90 percent CO<sub>2</sub> capture at less than a 35 percent increase in COE. It is anticipated that through well managed Federal research, development, and demonstration programs, a broad suite of cost-effective capture technologies will be available for commercial deployment by 2020 to respond to any future climate change regulations imposed upon the Nation's power generation sector.

Additional information related to DOE/NETL's EPEC Program is available at the following website: <a href="http://www.netl.doe.gov/technologies/coalpower/ewr/co2/index.html">http://www.netl.doe.gov/technologies/coalpower/ewr/co2/index.html</a>.

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#### References

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<sup>&</sup>lt;sup>1</sup> U.S. Department of Energy. Annual Energy Outlook 2008, *Revised to Include the Impact of H.R. 6*, "*Energy Independence and Security Act of 2007*" *Enacted in December 2007*. DOE Energy Information Administration, Washington, DC, Report #:DOE/EIA-0383, 2008.

<sup>&</sup>lt;sup>2</sup> International Energy Agency. *Energy Technology Perspectives*. IEA Head of Communication and Information Office, 9 rue de la Fédération, 75739 Paris Cedex 15, France, 2008.

<sup>&</sup>lt;sup>3</sup> Klara, S.M. et al. *Integrated collaborative technology development program for CO*<sub>2</sub> sequestration in geologic formations—United States Department of Energy R&D. Energy Conv. Manage. 44, 2699–2712, 2003.

<sup>&</sup>lt;sup>4</sup> U.S. Department of Energy. *Carbon Sequestration Technology Roadmap and Program Plan*. DOE Office of Fossil Energy's National Energy Technology Laboratory, Pittsburgh, PA, 2007. http://www.netl.doe.gov/publications/carbon\_seq/project%20portfolio/2007/2007Roadmap.pdf

http://www.netl.doe.gov/publications/carbon\_seq/project%20portfolio/2007/2007Roadmap.pdf.

5 U.S. Department of Energy. *Carbon Dioxide Capture from Existing Coal-Fired Power Plants*, DOE Office of Fossil Energy's National Energy Technology Laboratory, Pittsburgh, PA, DOE/NETL-401/110907, Revised November 2007. http://www.netl.doe.gov/energy-analyses/pubs/CO2%20Retrofit%20From%20Existing%20Plants%20Revised%20November%202007.pdf.

<sup>&</sup>lt;sup>6</sup> U.S. Department of Energy. *Pulverized Coal Oxy-combustion Power Plants, Vol.1: Bituminous Coal to Electricity*, DOE Office of Fossil Energy's National Energy Technology Laboratory, Pittsburgh, PA, DOE/NETL-2007/1291, Revision 2 August 2008. <a href="http://www.netl.doe.gov/energy-analyses/pubs/PC%200xyfuel%20Combustion%20Revised%20Report%202008.pdf">http://www.netl.doe.gov/energy-analyses/pubs/PC%200xyfuel%20Combustion%20Revised%20Report%202008.pdf</a>

<sup>&</sup>lt;sup>7</sup> Reddy, S.; Gilmartin, J. *Economine FG Plus* Technology for Post-Combustion CO<sub>2</sub> Capture. Presented at the Seventh Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 5-8, 2008.

<sup>&</sup>lt;sup>8</sup> Kishimoto, S. et al. *Current Status of MHI's CO2 Recovery Technology and Optimization of CO<sub>2</sub> Recovery Plant with a PC Fired Power Plant*. In Proceedings of the 9<sup>th</sup> International Conference on Greenhouse Gas Control Technologies, Washington, DC, November 16-20, 2008.

 $<sup>\</sup>frac{https://www4.events interactive.com/iea/viewpdf.esp?id=270005\&file=\%5C\%5Cserenity\%5CEP11\%24\%5CEventwin\%5CPool%5Coffice27\%5Cdocs\%5Cpdf\%5Cghgt%5F9Final00349\%2Epdf}{}$ 

<sup>&</sup>lt;sup>9</sup> International Energy Agency. *Improvement in Power Generation with Post-Combustion Capture of CO*<sub>2</sub>. IEA Greenhouse Gas R&D Programme, Report Number PH4/3, November 2004.

<sup>&</sup>lt;sup>10</sup> McCauley, K.J. et al. *Commercialization of Oxy-Coal Combustion: Applying Results of a Large 30MWth Pilot Project.* In Proceedings of the 9<sup>th</sup> International Conference on Greenhouse Gas Control Technologies, Washington, DC, November 16-20, 2008.

https://www4.eventsinteractive.com/iea/viewpdf.esp?id=270005&file=%5C%5Cserenity%5CEP11%24%5CEventwin%5CPool%5Coffice27%5Cdocs%5Cpdf%5Cghgt%5F9Final00309%2Epdf

The Stromberg, L. et al. *Update on Vattenfall's 30 MWth Oxyfuel Pilot Plant in Schwarze Plant.* In Proceedings of the 9<sup>th</sup> International Conference on Greenhouse Gas Control Technologies, Washington, DC, November 16-20, 2008. https://www4.eventsinteractive.com/iea/viewpdf.esp?id=270005&file=%5C%5Cserenity%5CEP11%24%5CEventwin%5CPool%5Coffice27%5Cdocs%5Cpdf%5Cghgt%5F9Final00949%2Epdf

 $\frac{https://www4.events interactive.com/iea/viewpdf.esp?id=270005\&file=\%5C\%5Cserenity\%5CEP11\%24\%5CEventwin\%5CPool\%5Coffice27\%5Cdocs\%5Cpdf\%5Cghgt\%5F9Final00288\%2Epdf$ 

 $\frac{https://www4.events interactive.com/iea/viewpdf.esp?id=270005\&file=\%5C\%5Cserenity\%5CEP11\%24\%5CEventwin\%5CPool\%5Coffice27\%5Cdocs\%5Cpdf\%5Cghgt\%5F9Final00606\%2Epdf}{2}$ 

http://www.netl.doe.gov/publications/proceedings/07/carbon-seq/start.htm

https://www4.eventsinteractive.com/iea/viewpdf.esp?id=270005&file=%5C%5Cserenity%5CEP11%24%5CEventwin%5CPool%5Coffice27%5Cdocs%5Cpdf%5Cghgt%5F9Final00721%2Epdf

Combustion Network 2<sup>nd</sup> Workshop, Windsor, CT, January 24-26, 2007. <a href="http://www.co2captureandstorage.info/docs/oxyfuel/MTG2Presentations/Session%2006/24%20-%20H.%20Andrus%20(Alstom).pdf">http://www.co2captureandstorage.info/docs/oxyfuel/MTG2Presentations/Session%2006/24%20-%20H.%20Andrus%20(Alstom).pdf</a>

<sup>&</sup>lt;sup>12</sup> Herzog, W. et al. *The Capture, Utilization and Disposal of Carbon Dioxide from Fossil Fuel-Fired Power Plants*, Final Report DOE Contract No. DE-FG02-92ER30194, July 1993.

<sup>&</sup>lt;sup>13</sup> Freeman, S. et al. *CO*<sub>2</sub> *Capture with Concentrated Aqueous Piperazine*. Presented at the Seventh Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 5-8, 2008.

<sup>&</sup>lt;sup>14</sup> Lu, Y. et al. Analysis of Heat Usage and Solvent Selection in Absorption Processes for Post-Combustion CO<sub>2</sub> Capture. Presented at the Seventh Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 5-8, 2008.

<sup>&</sup>lt;sup>15</sup> McLarnon, C.R.; Duncan, J.L. *Testing of Ammonia Based CO2 Capture with Multi-Pollutant Control Technology*. In Proceedings of the 9<sup>th</sup> International Conference on Greenhouse Gas Control Technologies, Washington, DC, November 16-20, 2008.

<sup>&</sup>lt;sup>16</sup> Wolsky, A.M. et al. *CO*<sub>2</sub> *Capture from the Flue Gas of Conventional Fossil-Fuel-Fired Power Plants*, Envir. Progress, Vol.13, No.3, p.214, August 1994.

<sup>&</sup>lt;sup>17</sup> Maginn, E. *Evaluation of Ionic Liquids in Post-Combustion CO<sub>2</sub> Capture*. Presented at the Seventh Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 5-8, 2008.

<sup>&</sup>lt;sup>18</sup> Gray, M.L. et. al. *Systematic Design of Immobilized Solid Amine Sorbents for the Capture of Carbon Dioxide*. Presented at the Sixth Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 7-10, 2007. <a href="http://www.netl.doe.gov/publications/proceedings/07/carbon-seq/start.htm">http://www.netl.doe.gov/publications/proceedings/07/carbon-seq/start.htm</a>

<sup>&</sup>lt;sup>19</sup> Nelson, T.O. et al. *The Dry Carbonate Process: Carbon Dioxide Recovery from Power Plant Flue gas.* In Proceedings of the 9<sup>th</sup> International Conference on Greenhouse Gas Control Technologies, Washington, DC, November 16-20, 2008.

<sup>&</sup>lt;sup>20</sup> Benin, A. et al. *Metal Organic Frameworks (MOFs) for CO<sub>2</sub> Capture*. Presented at the 2008 AIChE Spring National Meeting, New Orleans, LA, April 7-9, 2008.

<sup>&</sup>lt;sup>21</sup> Lin, H. et al. *The Membrane Solution to Global Warming*. Presented at the Sixth Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 7-10, 2007.

<sup>&</sup>lt;sup>22</sup> Trachtenberg, M.C. et al. *Membrane-Based, Enzyme-Facilitated, Efficient Carbon Dioxide Capture*. In Proceedings of the 9<sup>th</sup> International Conference on Greenhouse Gas Control Technologies, Washington, DC, November 16-20, 2008.

<sup>&</sup>lt;sup>23</sup> Suraniti, S.L. *Alstom Oxyfuel CFB Boilers: A Promising Option for CO2 Capture*. In Proceedings of the 9<sup>th</sup> International Conference on Greenhouse Gas Control Technologies, Washington, DC, November 16-20, 2008. https://www4.eventsinteractive.com/iea/viewpdf.esp?id=270005&file=%5C%5Cserenity%5CEP11%24%5CEventwin%5CPool%5Coffice27%5Cdocs%5Cpdf%5Cghgt%5F9Final00859%2Epdf

<sup>&</sup>lt;sup>24</sup> Van Hassel, B. et al. *Oxygen Transport Membrane Based OxyCombustion for CO<sub>2</sub> Capture from Coal Power Plants*. Presented at the Seventh Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 5-8, 2008.

<sup>&</sup>lt;sup>25</sup> Tian, H. et al. *Investigation of Chemical Looping Combustion of Coal Utilizing Various Oxygen Carriers*. Presented at the Seventh Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 5-8, 2008. <sup>26</sup> Andrus, H. *Chemical Looping Combustion – R&D Efforts of ALSTOM*. Presented at IEA GHG International Oxy-

<sup>&</sup>lt;sup>27</sup> Andrus, H. *ALSTOM Chemical Looping Combustion Coal Power Technology Development Prototype Phase IVA Kick-off Meeting*. Presented at the DOE/NETL Kickoff Meeting, Pittsburgh, PA, November 18, 2008. http://www.netl.doe.gov/technologies/coalpower/ewr/co2/pubs/Alstom%20Kickoff%2018Nov08.pdf

<sup>&</sup>lt;sup>28</sup> Baldwin, P. *Ramgen Power Systems Low-Cost*, *High-Efficiency CO*<sub>2</sub> *Compressor*. Presented at the Seventh Annual Conference on Carbon Capture and Sequestration, Pittsburgh, PA, May 5-8, 2008.